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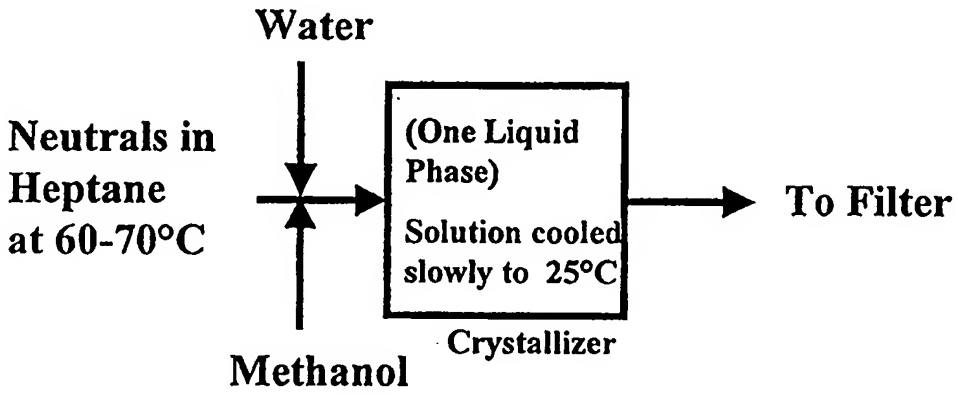
(54) Title: ISOLATION AND PURIFICATION OF STEROLS FROM NEUTRALS FRACTION OF TALL OIL PITCH BY DIRECT CRYSTALLIZATION, SINGLE PHASE



(57) Abstract

Isolation of the sterol component of the neutrals fraction of saponified tall oil pitch is disclosed. To the extracted neutrals, in a hydrocarbon (preferably heptane) phase, are added small amounts of water and an alcohol solvent, preferably methanol, at a relatively high temperature (preferably greater than 70 °C). The hydrocarbon/neutrals/alcohol/water solution is allowed to cool slowly, with agitation, to facilitate crystallization of sterols. The sterols are isolated and washed with hydrocarbon solvent.

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ISOLATION AND PURIFICATION OF STEROLS FROM NEUTRALS FRACTION OF TALL OIL PITCH BY DIRECT CRYSTALLIZATION, SINGLE PHASE

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention is related to methods of isolating and purifying the valuable constituents from Crude Tall Oil (CTO) recovered from the black liquor residue of wood pulping processes, primarily used in making paper. More particularly, the present invention is related to methods of extraction of valuable constituents from the bottoms, or pitch, fraction of distilled CTO. Most particularly, the present invention is related to methods of isolation and purification of extracted or distilled constituents of the neutrals fraction of CTO pitch which, upon said purification and subsequent modification, are useful as a dietary supplement in foods to reduce cholesterol levels in humans.

Description of Related Art

CTO and Crude Sulfate Turpentine (CST) are major, renewable, chemical raw materials obtained from the kraft (sulfate) pulping of various coniferous trees. Coniferous

trees, especially pine, contain resin acids in the free form, long chain fatty acids, and volatile terpenes. These materials, which are a major part of the wood extractives, are released from the wood during the kraft pulping process.

It has long been appreciated that the black liquor residue from wood pulping contains valuable chemicals, which make up the CTO, with various industrial applications. The black liquor contains the soaps of rosin and fatty acids, as well as sodium lignate and the spent cooking chemicals for reuse. On concentration of the spent pulping liquor, the sodium soap of these mixed acids rise to the surface and can be skimmed off. This material is referred to as "soap skimmings" or "tall oil soap." The soap skimmings are converted to CTO by reaction with sulfuric acid and then separated from the simultaneously-formed spent acid by batch cooking, continuous centrifuging, or continuous decanting. The CTO is normally divided into various fractions by distillation, which first extracts the pitch fraction. The depitched CTO is then separated into fractions of heads, tall oil rosin (TOR), tall oil fatty acids (TOFA), and distilled tall oil (DTO).

Concentrated in the pitch fraction of CTO is a neutral fraction thereof. A major ingredient of the neutral fraction of CTO pitch is a class of commercially significant compounds known as sterols, including sitosterol. It is commonly known, however, that a typical place to obtain these sterols is via solvent extraction of tall oil soap, which is practiced commercially in Scandinavia.

Recently, U.S. Patent No. 5,502,045 disclosed the use (by ingestion) of a ß-sitostanol fatty acid ester for reducing serum cholesterol level. The patent's assignee, Raisio, a Finnish manufacturer of foodstuffs, grain, and specialty chemicals, has developed a cholesterol-reducing margarine called Benecol®. The active, cholesterol-reducing ingredient in Benecol® is the claimed fat-soluble stanol ester which prevents cholesterol from being absorbed into the human digestive system. The stanol ester typically is produced from plant-derived sterols (phytosterols) via hydrogenation and trans-esterification reactions. Cholesterol reductions (LDL and HDL) of 10-15% are common for individuals with diets containing Benecol®.

Therefore, the value of recovering plant-derived sterols has become enhanced and the particular problems associated with recovering sitosterol from tall oil pitch worthy of investigation. A viable commercial process must achieve a high percent recovery of neutrals and/or sterols (greater than 70% recovery is preferable) and achieve high final sterol purity (higher than 95% is desirable). Past attempts to extract neutrals/sterols from one or more fractions of CTO are reported in the following patents:

Patent No.	Inventor	Title
US 2,499,430	Vogel et al.	"Obtaining Sterols of High Purity"
US 2,530,809	Christenson et al.	"Fractionation of Tall Oil"
US 2,530,810	Christensen, et al.	"Separation of Unsaponifiable Matter from Tall Oil Residue"
US 2,547,208	Hasselstrom et al.	"Method for the Refining of Tall Oil Residue"
US 2,715,638	Albrecht et al.	"Production of Sterols from Tall Oil Pitch"

Patent No.	Inventor	Title
US 2,835,682	Steiner et al.	"Sterol Recovery Process"
US 2,866,781	Chase et al.	"Separating Non-acids from Soap Stocks"
US 2,866,797	Berry et al.	"Improved Process of Isolating Sterols"
US 3,840,570	Julian et al.	"Process for Preparing Sterols from Tall Oil Pitch"
US 3,879,431	Clark et al.	"Purification of Sterols by Distillation"
US 3,965,085	Holmbom et al.	"Method for Refining of Soaps Using Solvent Extraction"
US 4,044,031	Johansson et al.	"Process for the Separation of Sterols"
US 4,124,607	Beaton et al.	"Preparation of Sterol Substrates for Bioconversion"
US 4,153,622	Lamminkari et al.	"Process for the Recovery of Beta-Sitosterol"
US 4,420,427	Hamunen	"Process for the Separation of Sterols or Mixtures of Sterols"
US 4,422,974	Hamunen	"Process for the Purification of Beta-Sitosterol Isolated from the Unsaponifiables in Crude Soap from the Sulphate Cellulose Process"
US 4,422,966	Amer	"Separation of Neutrals from Tall Oil Soaps"
US 4,496,478	Kulkarni et al.	"Process for Separating Unsaponifiables from Fatty and Rosin Acids"
US 4,524,024	Hughes	"Processes of Recovering Fatty Acids and Sterols from Tall Oil Pitch"
US 4,849,112	Barder et al.	"Adsorption Separation of Sterols from Tall Oil Pitch with Carbon Adsorbent"
US 4,935,168	Sjöberg et al.	"Process for the Preparation of Alcohols"
US 5,097,012	Thies et al.	"Solvent Extraction of Fatty Acid Stream with Liquid Water and Elevated Temperatures and Pressures"

These approaches, however, have failed to provide both a high percent recovery of neutrals and/or sterols and a high final sterol purity. It is an object of this invention, therefore, to provide a method for recovering the neutral fraction of saponified tall oil pitch and isolating a high percentage of the sterol component thereof. It is a further

object of this invention to obtain the isolated sterols at a high purity.

SUMMARY OF THE INVENTION

The above-stated objects of the invention are ultimately achieved by isolating the sterol component of the neutrals fraction of saponified tall oil pitch in the manner disclosed and claimed herein. The first step in the invention sterol isolation process is accomplished by extracting the neutrals from saponified tall oil pitch. Then the extracted neutrals phase in a hydrocarbon, preferably heptane, is mixed with amounts of water and an alcohol solvent, preferably methanol, at a relatively high temperature (preferably greater than 70°C). The hydrocarbon/neutrals/alcohol/water solution is allowed to cool slowly, with agitation, to facilitate crystallization of sterols. The sterols are isolated from the mother liquor and washed with solvent.

BRIEF DESCRIPTION OF THE DRAWING

The Figure represents a flow diagram of the claimed process of isolation and purification of sterols from single-solvent extraction neutrals of tall oil pitch by direct crystallization, single phase.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

Generally, the invention direct crystallization, single phase, process involves controlling the growth of sterol crystals from a solution of extracted, or distilled, tall oil pitch neutrals in a hydrocarbon solvent, preferably heptane, by adding small amounts of water and an alcohol solvent, preferably methanol (at a temperature greater than 70°C), with agitation. Sterol yields up to 68%, based on the weight of sterols recovered divided by the available sterols in the neutrals, were achieved. Also, purities of 95% were achieved, with negligible contamination by wax alcohols.

With reference to the Figure, the direct crystallization, single phase, process is seen to involve adding water and methanol to the relatively high temperature hydrocarbon/neutrals solution to result in a single liquid phase. The solution is allowed to cool slowly, during which time the sterols crystallize. The solution is then filtered to recover the sterol crystals.

In a preferred embodiment of the invention process, the first step involves dissolving concentrated (solventless) single-solvent extraction neutrals of a tall oil pitch fraction in a heptane. (For the purposes of the following examples, solventless single-solvent extraction neutrals are prepared in the laboratory; but, in actual plant operation, the neutrals remain in residual heptane from the flash vessel following the single-solvent extraction operation.) A temperature of 50-60°C

is sufficient to dissolve the neutrals in the lab; however, optimization of the invention process involves raising the temperature of the heptane stream/phase to greater than 70°C. Next, the small amounts of methanol and water are added while the mixture is still at 70°C. The parts heptane:methanol:water ratio is 2-5:0.05-0.15:0.05-0.15, preferably 2.5:0.10:0.10, respectively. The single-phase solution is allowed to cool slowly with sufficient agitation to keep the slurry well stirred throughout. Finally, the sterol crystals are filtered using a jacketed Buchner funnel, and the resulting filter cake is washed with copious amounts of heptane. The jacketed Buchner funnel is kept at near 40°C using a water bath. This keeps the temperature of the filter cake from cooling excessively during filtration, which can lead to precipitation of wax alcohols. Final crystallation temperature is from 25-35°C, preferably 30°C.

The following examples are representative of the invention process:

Multiple experiments were conducted according to the description of the invention process set forth above, and data were tabulated for various combinations of high and low values for three variables in Table I and were based on a heptane to neutrals ratio of 3.5:1.0.

TABLE I

Example	Methanol (parts)	Water (parts)	Final Temp (°C)	Mass Yield (%)	Sterol Yield (%)	Purity (%)
1	0.1	0.1	30	71.9	68.4	95.1
2	0.1	0.05	25	66.8	59.4	89
3	0.05	0.1	30	71.2	66.9	93.9
4	0.05	0.05	30	62.3	58.6	94.2
5	0.1	0.05	30	67	63.3	94.4
6	0.1	0.1	25	72.4	68.5	94.6
7	0.05	0.1	25	70.3	65.2	92.8
8	0.05	0.05	25	57.9	53.2	91.8

The key variables and ranges for Examples 1-8 are listed in Table II.

Table II

Factor[a]	Low	High
Water Content (parts)	0.05	0.10
Methanol Content (parts)	0.05	0.10
Final Crystallization Temperature (°C)	25	30

(a) Parts refers to the relative weight ratio of the variable to the amount of neutrals used in the experiment.

The data from Table I show that mass yields ranged from 57.9 - 72.4%, sterol yields ranged from 53.2 - 68.5%, and sterol purities ranged from 89.0 - 95.1%. Two experimental conditions (Examples 1 and 6) gave sterol yields and purities of approximately 68% and 95%, respectively. Others were close to those levels. Statistical analyses of the data using StatGraphics® software show that all of the variables were

statistically significant in affecting sterol yield; however, none were significant in affecting sterol purity.

In another set of experiments (Examples 9-28), the direct crystallization-single phase process proceeded as described above, except combinations of high and low values of four variables were included as indicated in Table III.

Table III

Factor[a]	Low	High	Center Point
Heptane Content parts)	2.0	5.0	2.5
Methanol Content (parts)	0.05	0.15	0.10
Water Content (parts)	0.05	0.15	0.10
Final Crystallization Temperature (°C)	25	35	30

(*) Parts refers to the relative weight ratio of the variable to the amount of neutrals used in the experiment.

The results from Examples 9-28 are shown in Table IV.

TABLE IV

Run	Heptane (parts)	Methanol (parts)	Water (parts)	Final Temp. (°C)	Mass Yield (%)	Sterol Yield (%)	Purity (%)	Wax Alcohol (% by GC)	Non-Elutables (%)
9	3.5	0.1	0.1	30	66.2	62.6	96	0	1.5
10	2	0.15	0.15	35	64.4	62.1	96.3	0	1.3
11	2	0.15	0.05	35	56.8	54.5	96	0	1.8
12	5	0.05	0.05	35	52.8	50.5	95.6	0	2.2
13	2	0.05	0.05	25	69.8	66.8	95.6	0.2	1.7
14	2	0.15	0.15	25	71.9	68.3	95	0.6	2.1
15	2	0.15	0.05	25	64.4	61.4	95.4	0.2	2.2
16	5	0.15	0.15	35	52.2	50.7	97.1	0	0.6
17	5	0.05	0.05	25	68	65	95.5	0.1	2.2
18	3.5	0.1	0.1	30	58.5	55.3	94.6	0	2.8
19	5	0.05	0.15	35	51.7	49.1	94.9	0	2.8
20	2	0.05	0.15	35	66.8	62.7	93.8	0.5	3.3
21	5	0.15	0.15	25	59.4	55	92.6	0	5.2
22	2	0.05	0.05	35	58.8	57.1	97.1	0	0.6
23	5	0.05	0.15	25	63.3	61.2	96.7	0.1	0.9
24	5	0.15	0.05	25	53.1	51.8	97.6	0	0.2
25	2	0.05	0.15	25	72.4	65.5	90.5	2.5	4.5
26	5	0.15	0.05	35	31.7	30.3	95.7	0	1.8
27	3.5	0.1	0.1	30	57.2	55.4	96.9	0	0.5
28	3.5	0.1	0.1	30	59.1	55.3	93.5	0	4.5
			Center Point Mean and Standard Deviation -		60.0 ± 3.1%	57.2± 3.1%	95.3 ± 1.3%	0%	2.3 ± 1.5%

Mass yields ranged from 31.7 - 72.4%, sterol yields ranged from 30.3 - 65.5%, sterol purities ranged from 90.5 - 97.6%. Center point conditions gave mass yields of 60.0 ± 3.1%, sterol yields of 57.2 ±3.1%, sterol purities of 95.3 ±1.3%, wax alcohol contaminations of 0%, and non-elutables contents of 2.3 ± 1.5%. Like Examples 1 and 6 in Table I, one of the experimental conditions (Example 14) gave sterol yields and purities (68% and 95%, respectively). Again, others were close to those levels. Statistical analyses of the data using StatGraphics® software show that all of the variables were statistically significant

in affecting mass yield and sterol yield; however, none were significant in affecting sterol purity. This time, the lower values were favorable for heptane content and final crystallization temperature for both mass yield and sterol yield. Like in Table I, none of the variables statistically affected the sterol purity results. Similarly, none of the variables affected the non-elutables content in the sterols product. Wax alcohol contamination was enhanced with the lower heptane loadings. The purity was high (all near 95%) and non-elutables were low for all of the runs in this experimental design.

The subject matter of the invention is:

(1) A method for the isolation of sterols from sulfate pulping process tall oil pitch comprising the steps of:

(a) saponifying the tall oil pitch;

(b) extracting the neutral fraction from the saponified tall oil pitch;

(c) blending a hydrocarbon solution of the neutrals with a 1-3:1-3 mixture, respectively, of an alcohol solvent and water at a temperature greater than 50°C;

(d) the blended solution is allowed to cool to a final temperature from about 20°C to about 40°C to produce sterol crystals;

(e) the sterol crystals are isolated from the cooled solution.

(2) the method of (1) wherein the extraction neutrals of tall oil pitch are derived by a process selected from the group

consisting of single-solvent extraction and distillation;

(3) the method of (1) wherein the hydrocarbon solvent is selected from the group consisting of straight- and branched-chain hydrocarbons with from 5 to 10 carbons;

(4) the method of (3) wherein the hydrocarbon solvent is selected from the group consisting of pentane, hexane, heptane, and iso-octane;

(5) the method of (1) wherein the alcohol solvent is an aliphatic alcohol; and

(6) the method of claim 5 wherein the alcohol solvent is selected from the group of aliphatic alcohols consisting of methanol, ehtanol, butanol, and iso-propanol.

(7) the method of claim 1 wherein the temperature in step (a) is greater than 60°C.

(8) the method of claim 1 wherein the temperature in step (a) is greater than 70°C.

Modifications to this invention will occur to those skilled in the art. Therefore, it is to be understood that this invention is not necessarily limited to the particular embodiments disclosed; rather, it is intended to cover all modifications which are within the true spirit and scope of this invention, as disclosed and claimed herein.

What is claimed is:

1. A method for the isolation of sterols from sulfate pulping process tall oil pitch comprising the steps of:

(a) saponifying the tall oil pitch;

(b) extracting the neutral fraction from the saponified tall oil pitch;

(c) blending a hydrocarbon solution of the neutrals with a 1-3:1-3 mixture, respectively, of an alcohol solvent and water at a temperature greater than 50°C;

(d) the blended solution is allowed to cool to a final temperature from about 20°C to about 40°C to produce sterol crystals;

(e) the sterol crystals are isolated from the cooled solution.

2. The method of claim 1 wherein the extraction neutrals of tall oil pitch are derived by a process selected from the group consisting of single-solvent extraction and distillation.

3. The method of claim 1 wherein the hydrocarbon solvent is selected from the group consisting of straight- and branched-chain hydrocarbons with from 5 to 10 carbons.

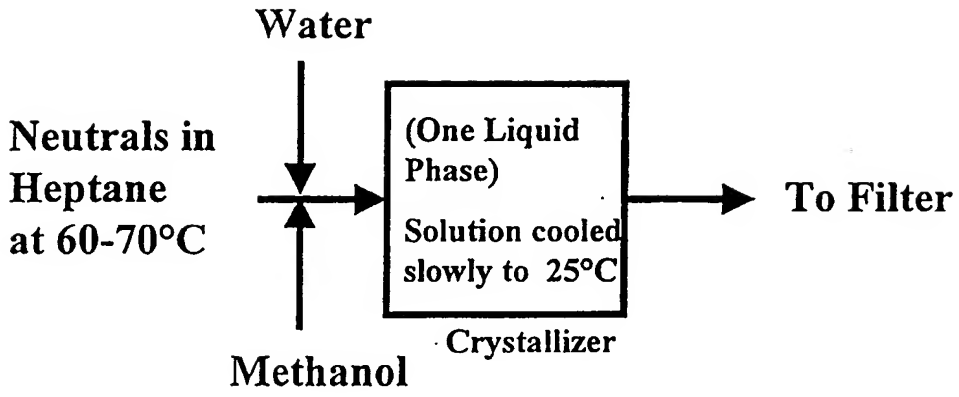
4. The method of claim 3 wherein the hydrocarbon solvent is selected from the group consisting of pentane, hexane, heptane, and iso-octane.

5. The method of claim 1 wherein the alcohol solvent is an aliphatic alcohol.

6. The method of claim 5 wherein the alcohol solvent is selected from the group of aliphatic alcohols consisting of methanol, ehtanol, butanol, and iso-propanol.

7. The method of claim 1 wherein the temperature in step (a) is greater than 60°C.

8. The method of claim 1 wherein the temperature in step (a) is greater than 70°C.


Water
Neutrals in
Heptane
at 60-70°C
(One Liquid
Phase)
Solution cooled
slowly to 25°C
Crystallizer
To Filter
Methanol

Figure

INTERNATIONAL SEARCH REPORT

Inter 'onal Application No
PCT/US 99/14138

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07J9/00 C11B13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07J C11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2 530 810 A (R. M. CHRISTENSON ET AL) 21 November 1950 (1950-11-21) examples A,IX,,X ---	1-8
Y	US 4 044 031 A (JOHANSSON AKE ALLAN ET AL) 23 August 1977 (1977-08-23) example 1 ---	1-8
Y	US 3 691 211 A (JULIAN DONALD V) 12 September 1972 (1972-09-12) whole document, in particular example 1 and claim 1 ---	1-8
Y	US 3 840 570 A (JULIAN D) 8 October 1974 (1974-10-08) whole document, in particular claim 1 and examples 1, 2 --- -/--	1-8

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
28 September 1999	13/10/1999

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Inter 'onal Application No
PCT/US 99/14138

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 524 024 A (HUGHES RICHARD E) 18 June 1985 (1985-06-18) example 3	1-8
Y	US 4 298 539 A (KOSKENNISKA LASSE A) 3 November 1981 (1981-11-03) column 1, paragraph 3; example 1	1-8
Y	EP 0 057 075 A (FARMOS OY) 4 August 1982 (1982-08-04) the whole document	1-8
Y	DATABASE PAPERCHEM2 'Online! KARPUS, G. G. ET AL: "COMPARISON OF LTA (LENINGRAD ACADEMY OF WOOD TECHNOLOGY) METHODS FOR OBTAINING STEROIDS FROM SULFATE SOAP AND TALL OIL PITCH" retrieved from STN Database accession no. 6176 XP002116668 abstract & IZV. VUZ, LESNOI ZH., (1976) VOL. 19, NO. 1, PP. 115-118. 'RUSS.!.,	1-8
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INTERNATIONAL SEARCH REPORT

.ormation on patent family members

Inter ·onal Application No
PCT/US 99/14138

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